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Statics and dynamics of fluids in nanotubes

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Abstract. The purpose of this article is to study the statics and dynamics of nanotubes by using the methods of continuum mechanics. The nanotube can be filled with only a liquid or a vapour phase according to the physicochemical characteristics of the wall and to the disjoining pressure associated with the liquid and vapour mother bulks of the fluid, regardless of the nature of the external mother bulk. In dynamics, flows through nanotubes can be much more important than classical Poiseuille flows. When the external mother bulk is of vapour, the flow can be a million times larger than the classical flows when slippage on wall does not exist.

Keywords: Density distribution in nanotube, Nanotube flows, Fluid-solid interactions.

MSC 2000 Classification: 82D80, 74F10

1 Introduction

On one hand, it is well documented in the modern literature that the conventional laws of capillarity are not adequate when applied to fluids confined by porous materials [3]. On the other hand, the technical development of sciences allows us to observe phenomena at length scales of a very few number of nanometres. This nanophysics allows to infer applications in numerous fields, including medicine and biology. Iijima often cited as the discoverer of carbon nanotubes [21], was fascinated by Krätschmer *et al*' Nature paper [23], and decided to launch out into a detailed study of nanomaterials. The recent applications revealed new behaviors that are often surprising and essentially different from those usually observed at macroscopic scale but also at microscopic scale [20]. Nonetheless, simple models proposing qualitative behaviors need to be developed in the different fields of nanosciences; our aim is to investigate the fluid-solid interaction in static as well as in dynamic conditions by differential calculus in continuum mechanics.
As it was pointed out in experiments, the density of liquid water changes in narrow pores [2]; an analytic asymptotic expression was obtained with an approximation of London potentials for liquid-liquid and solid-liquid interactions,

which yields the surface interaction energy [15]. With the aim to propose an analytic expression of the density for liquid films with a nanometer thickness near a solid wall, we add together the interaction energy at the solid surface to a density-functional at the liquid-vapour interface and a square-gradient functional which represents the volume free energy of the fluid [14, 16]. The obtained functional allows to get a differential equation and boundary condition which yield the density profile in cylindrical nanotubes.
For shallow water, the flows of liquids on solids are mainly represented by using the Navier-Stokes equations associated with the adherence condition at the walls [29]. Recent experiments in nanofluidics seem to prove that the adherence condition is often disqualified [10]. So, we can draw consequences which differ from results of classical models; the model we are presenting reveals an essential difference between the flows of microfluidics and those of nanofluidics [33]. The simple laws of scales cannot be only taken into account. The film-solid interactions are accounted for in terms of the disjoining pressure. This concept of disjoining pressure has been introduced by Derjaguin in 1936 as the difference between the pressure in a phase adjacent to a surface confining it and the pressure in the bulk of this phase [11, 18]. We have previously seen that the gradient of thickness along layers creates a gradient of disjoining pressure that induces driving forces along the layer [19]. Moreover, we had noticed that the stability criterion of the flow issued from the equation of motions fits with the results of Derjaguin's school [19].
The liquid flows through nanotubes also depend on the wetting conditions on the wall. Some phase transitions can appear and drastically change the liquid flows through nanotubes. Since fifteen years the literature is abundant about nanotube technology and flows inside nanotubes [26].

The aim of this paper is not to redo the literature but to emphasis on liquid compressibility near solid walls in nanoscale conditions. We consider a nanotube made up of a cylindrical hollow tube whose diameter is of some nanometres. The length of the nanotube is microscopic and the edge of the cylinder is a solid made out of carbon or other materials [20]. The nanotube is immersed in a liquid or a vapour made up of the same fluid. The fluid fills the interior of the nanotube. The fluid is modeled by a van der Waals fluid [22, 35] for which the surdeformations are taken into account (we called *capillary fluid* or *Cahn and Hilliard fluid* [6, 14]). The volume free energy of the fluid is a function not only of the density but also of the gradient of density. The conditions on the wall take account of the fluid density at its immediate proximity [15]. We first recall the equations of equilibrium and motion of capillary fluids [14]. These fluids can be modeled on the interfaces as the fluids in the immediate vicinity of solid media [15]. In liquid or vapour phase, it is possible to express the chemical potential with a development in a linear form taking account of the isothermal sound velocity values in the bulks [18]. The main expansions of the free energy in liquid and vapour phases are deduced. In nanofluidics, the interactions between fluid and solid wall dominate over the hydrodynamic behaviour of the fluid [2]. Boundary conditions are embedding effects; they are

expressed thanks to a surface energy associated with a molecular model in mean field theory [16].

In the case of cylindrical geometry, a differential equation with respect to the fluid density is obtained. Then, the profile of the fluid density in a cylinder can be deduced. The result is applied to nanotubes when the diameter ranges from a little number of nanometres to one hundred nanometres. Depending on the disjoining pressure between liquid and vapour bulks and on the wettability of the nanotube wall, we can forecast when the fluid inside the nanotube is liquid or vapour; the wall effect is dominant. The case of liquid and vapour separated by an interface is not possible when the nanotube diameter is smaller than one hundred nanometres and a liquid is generally found inside the nanotube.
Recently, it was showed, by using nonequilibrium molecular dynamics simulations, that liquid flow through a membrane composed of an array of aligned carbon nanotubes is four to five orders of magnitude faster than it would be predicted from conventional fluid-flow theory [25]. These high fluid velocities are possible because of a frictionless surface at the nanotube wall [27]. Majunder *et al* quote slip lengths on the order of microns for their experiments with nanometer size pores [25]. The extremely large slip lengths measured in carbon nanotubes greatly reduce the fluidic resistance and nanoscale structures could mimic extraordinarily fast flow possible in biological cellular channels [5]. By calculating the variation of water viscosity and slip length as a function of the nanotubes diameter, the results can be fully explained in the context of continuum fluid mechanics [34].
In this paper we recalculate the flows through nanotubes by using a Navier-Stokes equation but, due to the slip condition and the Navier length, it is possible to forecast an important difference between classical Poiseuille flows and flows through nanotubes. The calculations associated with the physicochemical quality of the nanotube allow to forecast if the fluid phase inside the tube is constituted of liquid or vapour. A spectacular effect must appear when the mother bulk outside the nanotube is constituted of vapour; in this case, the volume flow through the nanotube is multiplied by a factor of the order of one million with respect to the Poiseuille flow and the velocity field through the nanotube may be very important.

2 Equation of motion and boundary conditions for a capillary fluid

2.1 Case of conservative fluid

The second gradient theory [12, 13], conceptually more straightforward than the Laplace theory, can be used to elaborate a theory of capillarity [28]. The theory can also be used to investigate domains where the fluids are strongly inhomogeneous as in the immediate vicinity of solid walls where intermolecular forces are dominant between fluid and solid with respect to fluid interactions. By this simple way, the only change with respect to compressible fluids is that

the specific internal energy is not only a function of the density ρ, of the specific entropy s, but also of $\operatorname{grad}\rho$. Consequently, the specific internal energy ε characterizes both the compressibility and the surdeformation of the fluid,

$$\varepsilon = f(\rho, s, \beta), \quad \text{where} \quad \beta = (\operatorname{grad}\rho)^2.$$

We recall the main results of *capillary fluids* already obtained in the literature [14, 17, 32]:

The equation of conservative motions of such *capillary fluids* is

$$\rho\,\mathbf{a} = \operatorname{div}\boldsymbol{\sigma} - \rho\,\operatorname{grad}\Omega, \tag{1}$$

where $\mathbf{a}$ denotes the acceleration vector, Ω the extraneous force potential and $\boldsymbol{\sigma}$ the total stress tensor. The total stress tensor is

$$\boldsymbol{\sigma} = -p\,\mathbf{I} - \lambda\,(\operatorname{grad}\rho)(\operatorname{grad}\rho)^T \quad \text{or} \quad \sigma_{ij} = -p\,\delta_{ij} - \lambda\,\rho_{,i}\rho_{,j}\,,\ i,j \in \{1,2,3\} \tag{2}$$

where ^{T} denotes the transposition, with

$$\lambda \equiv 2\,\rho\,\varepsilon'_\beta \qquad \text{and} \qquad p \equiv \rho^2\varepsilon'_\rho - \rho\,\operatorname{div}(\lambda\,\operatorname{grad}\rho).$$

It should be noted that ε'_s is the Kelvin temperature expressed as a function of ρ, s and β. It appears that only the scalar λ accounts for surdeformation effects. As ε does, the scalar λ depends on ρ, s and β. For the surface tension study based on the gas kinetic theory, Rocard obtained the expression (2) for the stress tensor but with λ constant [31]. If λ is constant, the specific energy ε reads

$$\varepsilon(\rho, s, \beta) = \alpha(\rho, s) + \frac{\lambda}{2\rho}\,\beta,$$

and the *second gradient* term $\lambda\,\beta/(2\,\rho)$ is simply added to the specific internal energy $\alpha(\rho, s)$ of the classical compressible fluid. The pressure of the compressible fluid is $P \equiv \rho^2\alpha'_\rho$ and the temperature is $T \equiv \alpha'_s$. Consequently,

$$p = P - \lambda\left(\frac{\beta}{2} + \rho\,\Delta\rho\right).$$

For the thermodynamical pressure P, Rocard and others authors use the van der Waals pressure

$$P = \rho\,\frac{R\,T}{1 - b\rho} - a\rho^2$$

or other similar laws [31]. It should be noted that if λ is constant, there exits a relation independent of grad ρ between T, ρ and s.

2.1.1 Case λ constant

Equation (2) yields

$$\sigma_{ij} = -P\,\delta_{ij} + \lambda\left\{\left(\frac{1}{2}\,\rho_{,k}\rho_{,k} + \rho\rho_{,kk}\right)\delta_{ij} - \rho_{,i}\rho_{,j}\right\}.$$

Let us denote $\omega = \Omega - \lambda\,\Delta\rho$, then Eq. (1) reads

$$\rho\,\mathbf{a} + \operatorname{grad} P + \rho \operatorname{grad}\omega = 0. \tag{3}$$

This relation is similar to the perfect fluid case; the term ω involves all capillarity effects. From $\sigma_{ij,j} = -P_{,i} + \lambda\,\rho\rho_{,ijj}$ and by neglecting the extraneous forces, we obtain:

$$\rho\,\mathbf{a} + \operatorname{grad} P = \lambda\,\rho\ \operatorname{grad}\Delta\rho.$$

2.1.2 Thermodynamic form of the equation of motion

Commonly - and not only when λ is constant - the equation of motion (1) can be written in a thermodynamic form

$$\mathbf{a} = \theta \operatorname{grad} s - \operatorname{grad}(h + \Omega), \quad \text{with} \quad h = \varepsilon + \frac{p}{\rho}\,. \tag{4}$$

In the non-capillarity case ($\varepsilon'_\beta = 0$ or $\varepsilon = \alpha(\rho, s)$), Eq. (4) is well-known. When T is constant, Eq. (4) yields

$$\mathbf{a} + \operatorname{grad}(\pi + \Omega) = 0, \quad \text{with} \quad \pi = h - T\,s\,. \tag{5}$$

The potentials h and π are the *generalized enthalpy and the chemical potential* of the capillary fluid.

2.2 Case of viscous fluid

In the case of viscous fluids, the equation of motion includes not only the stress tensor $\boldsymbol{\sigma}$, but also the viscous stress tensor $\boldsymbol{\sigma}_v$ written in the form:

$$\boldsymbol{\sigma}_v = \eta\ \mathtt{tr}\,\boldsymbol{D} + 2\,\kappa\,\boldsymbol{D},$$

where $\boldsymbol{D}$ is the deformation tensor, symmetric gradient of the velocity field and η and κ are constant in the viscous linear case. Of course in second gradient theory, it would be coherent to add terms accounting for the influence of higher order derivatives of the velocity field to the viscous stress tensor $\boldsymbol{\sigma}_v$; the surdeformation of density comes from wall effects but the variations of velocity are negligible and the second derivatives are not taken into account. Equation (1) is modified by adding the forces associated with the viscosity and we obtain

$$\rho\,\mathbf{a} = \operatorname{div}(\boldsymbol{\sigma} + \boldsymbol{\sigma}_v) - \rho \operatorname{grad}\Omega\,.$$

For viscous fluid, Eq. (3) reads

$$\rho\,\mathbf{a} + \operatorname{grad} P + \rho \operatorname{grad}(\Omega - \lambda\,\Delta\rho) - \operatorname{div}\boldsymbol{\sigma}_v = 0. \tag{6}$$

2.3 Boundary conditions at a solid wall

The forces acting between liquid and solid range over a few nanometres but can be simply described by a special surface energy. This energy is not the total interfacial energy which results from the direct fluid/solid contact; another energy results from the distortion in the fluid density profile near the wall. For a solid wall not too curved at a molecular scale, the total surface free energy φ is developed as [15]:

$$\varphi(\rho_{_S}) = -\gamma_1 \rho_{_S} + \frac{1}{2}\,\gamma_2\,\rho_{_S}^2. \tag{7}$$

Here $\rho_{_S}$ denotes the limit value of the fluid density at the surface (S); the constants γ_1, γ_2 as the constant λ are positive. In the mean field approximation of molecular theory they are:

$$\gamma_1 = \frac{\pi c_{ls}}{12\delta^2 m_l m_s}\,\rho_{sol}, \quad \gamma_2 = \frac{\pi c_{ll}}{12\delta^2 m_l^2},$$

with

$$\lambda = \frac{2\pi c_{ll}}{3\sigma_l\, m_l^2},$$

where m_l et m_s denote the molecular masses of fluid and solid, respectively, ρ_{sol} is the solid density; other constants come from London potentials of liquid-liquid and liquid-solid interactions expressed in the form

$$\begin{cases} \varphi_{ll} = -\dfrac{c_{ll}}{r^6}\,, & \text{when } r > \sigma_l \text{ and } \quad \varphi_{ll} = \infty \text{ when } \quad r \le \sigma_l\,, \\ \varphi_{ls} = -\dfrac{c_{ls}}{r^6}\,, & \text{when } r > \delta \text{ and } \quad \varphi_{ls} = \infty \text{ when } \quad r \le \delta\,, \end{cases}$$

where c_{ll} et c_{ls} are two positive coefficients associated with Hamaker constants, σ_l and σ_s denote the molecular diameters for the fluid and the solid, $\delta = \frac{1}{2}\,(\sigma_l + \sigma_s)$.

The boundary condition for the density at the solid wall (S) associated with the free surface energy (7) is calculated in [16]:

$$\lambda \left(\frac{d\rho}{dn}\right)_{|S} + \varphi'(\rho_{_S}) \;= 0, \tag{8}$$

where n is the external normal direction to the fluid.

3 The chemical potential in liquid and vapour phases

The chemical potential of a compressible fluid at temperature T is denoted by $\mu_{_0}$. Due to the equation of state $P \equiv P(\rho, T)$, it is possible to express $\mu_{_0}$ as a function of ρ (and T). At a given temperature, the volume free energy g_0

associated with μ_0 verifies $g_0'(\rho) = \mu_0(\rho)$. Due to the fact μ_0 and g_0 are defined to an additive constant, we add the conditions

$$\mu_0(\rho_l) = \mu_0(\rho_v) = 0 \quad \text{and} \quad g_0(\rho_l) = g_0(\rho_v) = 0,$$

where ρ_l and ρ_v are the fluid densities in the liquid and vapour bulks corresponding to the plane liquid-vapour interface at temperature T.
The expressions of the two thermodynamical potentials μ_0 and g_0 can be expended at the first order near the liquid and vapour bulks, respectively

$$\mu_0(\rho) = \frac{c_l^2}{\rho_l}(\rho - \rho_l) \qquad \text{and} \qquad \mu_0(\rho) = \frac{c_v^2}{\rho_v}(\rho - \rho_v),$$

$$g_0(\rho) = \frac{c_l^2}{2\rho_l}(\rho - \rho_l)^2 \qquad \text{and} \qquad g_0(\rho) = \frac{c_v^2}{2\rho_v}(\rho - \rho_v)^2,$$

where c_l and c_v are the isothermal sound velocities in the liquid and vapour bulks [18]. Consequently, at temperature T, it is possible to obtain the connection between the liquid bulk of density ρ_{l_b} and the vapour bulk of density ρ_{v_b} corresponding to curved interfaces (as for spherical bubbles and droplets [8, 9]): we call them the mother bulk densities. These equilibria do not obey the Maxwell rule [1], but the values of the chemical potential in the two mother bulks are equal:

$$\mu_0(\rho_{l_b}) = \mu_0(\rho_{v_b}). \tag{9}$$

Consequently, we define $\mu_{l_b}(\rho)$ and $\mu_{v_b}(\rho)$ at temperature T as:

$$\mu_{l_b}(\rho) = \mu_0(\rho) - \mu_0(\rho_{l_b}) \equiv \mu_0(\rho) - \mu_0(\rho_{v_b}) = \mu_{v_b}(\rho).$$

An expansion to the first order near the liquid and vapour bulks yields

$$\mu_{l_b}(\rho) = \frac{c_l^2}{\rho_l}\left(\rho - \rho_{l_b}\right) \qquad \text{and} \qquad \mu_{v_b}(\rho) = \frac{c_v^2}{\rho_v}\left(\rho - \rho_{v_b}\right)$$

and due to relation (9),

$$\frac{c_l^2}{\rho_l}\left(\rho_{l_b} - \rho_l\right) = \frac{c_v^2}{\rho_v}\left(\rho_{v_b} - \rho_v\right)$$

which clarifies the connection between ρ_{l_b} and ρ_{v_b}.
To the chemical potential $\mu_{l_b}(\rho) \equiv \mu_{v_b}(\rho)$ at temperature T, we associate the volume free energies $g_{l_b}(\rho)$ and $g_{v_b}(\rho)$ that are null for ρ_{l_b} and ρ_{v_b}, respectively:

$$g_{l_b}(\rho) = g_0(\rho) - g_0(\rho_{l_b}) - \mu_0(\rho_{l_b})(\rho - \rho_{l_b}),$$

$$g_{v_b}(\rho) = g_0(\rho) - g_0(\rho_{v_b}) - \mu_0(\rho_{v_b})(\rho - \rho_{v_b}).$$

The free energies $g_{l_b}(\rho)$ and $g_{v_b}(\rho)$ are the reference free energies associated with the liquid and vapour mother bulks. The reference free energy $g_{l_b}(\rho)$ differs from $g_{v_b}(\rho)$ by a constant. Moreover, the volume free energies are expanded as

$$g_{l_b}(\rho) = \frac{c_l^2}{2\rho_l}\left(\rho - \rho_{l_b}\right)^2 \qquad \text{and} \qquad g_{v_b}(\rho) = \frac{c_v^2}{2\rho_v}\left(\rho - \rho_{v_b}\right)^2.$$

4 Liquid and vapour densities in a nanotube

A nanotube is constituted of a hollow cylinder of length size ℓ and of small diameter $d = 2R$, $(d/\ell \ll 1)$. We consider solid walls with a large thickness with regards to molecular dimensions such that the surface energy verifies an expression in form (7). We assume that a capillary fluid is a convenient model to represent fluids inside the nanotube.
At equilibrium, far from the nanotube tips and by neglecting the external forces, the profile of density is solution of Eq. (5) with $\mathbf{a} = 0$ and $\pi = \mu_{_0} - \lambda\,\Delta\rho$:

$$\lambda\,\Delta\rho = \mu_{_0}(\rho) - C, \tag{10}$$

where C is an additional constant. The value of C is associated with the density value in the mother bulk outside the nanotube (where $\Delta\rho = 0$) [11]. Consequently, the reference density value $\rho_{_{ref}}$ may be chosen as $\rho_{_{l_b}}$ or $\rho_{_{v_b}}$.
We consider the cases when exclusively liquid or vapour fill up the nanotube; the mother bulk can be as well liquid as vapour. The profile of density is given by the differential equation:

$$\lambda\left(\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr}\right) - \frac{c^2_{_{ref}}}{\rho_{_{ref}}}\,u = 0, \qquad \text{with} \quad u = \rho - \rho_{_{ref}}, \tag{11}$$

where $c_{_{ref}}$ is the isothermal sound velocity associated with liquid mother bulk (respectively vapour mother bulk) when the liquid phase fills up the nanotube (respectively vapour phase). In cylindrical coordinates, r denotes the radial coordinate. The reference length is

$$\delta_{_{ref}} = \sqrt{\lambda\,\rho_{_{ref}}/c^2_{_{ref}}}\,.$$

We denote by x the dimensionless variable such that $r = \delta_{_{ref}}\,x$. Equation (11) reads

$$\frac{d^2u}{dx^2} + \frac{1}{x}\frac{du}{dx} - \;u = 0.$$

The solutions of Eq. (4) in classical expansion form $u = \sum_{n=0}^{\infty} a_n x^n$ yield:

$$\sum_{n=2}^{\infty} n^2\,a_n\,x^{n-2} - a_{n-2}\,x^{n-2} = 0 \quad \Longrightarrow \quad n^2\,a_n = a_{n-2}\,.$$

Due to the symmetry at $x = 0$, the odd terms are null and consequently,

$$u = a_{_0}\sum_{p=0}^{\infty}\;\frac{1}{4^p\,(p\,!)^2}\;x^{2p}\,.$$

The series has an infinite radius of convergence. Let us define the quantities

$$\begin{aligned} f(x) &= \sum_{p=0}^{\infty} \frac{1}{4^p\,(p!)^2}\; x^{2p}, \\ h(x) &\equiv f'(x) = \sum_{p=1}^{\infty} \frac{2p}{4^p\,(p!)^2}\; x^{2p-1}, \\ k(x) &\equiv f''(x) = \sum_{p=1}^{\infty} \frac{2p\,(2p-1)}{4^p\,(p!)^2}\; x^{2p-2}. \end{aligned}$$

Consequently, $u = a_{_0}\, f(r/\delta_{_{ref}})$. The boundary condition (8) at $x = R/\delta_{_{ref}}$ is:

$$\lambda \frac{du}{dx} = \gamma_1 - \gamma_2\,\rho \qquad \text{or} \qquad a_{_0} = \frac{\delta_{_{ref}}\,\left(\gamma_1 - \gamma_2\,\rho_{_{ref}}\right)}{\lambda\, h\left(\frac{R}{\delta_{_{ref}}}\right) + \gamma_2\,\delta_{_{ref}}\, f\left(\frac{R}{\delta_{_{ref}}}\right)}$$

and the density profile reads

$$\rho = \rho_{_{ref}} + \frac{\delta_{_{ref}}\,\left(\gamma_1 - \gamma_2\,\rho_{_{ref}}\right)}{\lambda\, h\left(\frac{R}{\delta_{_{ref}}}\right) + \gamma_2\,\delta_{_{ref}}\, f\left(\frac{R}{\delta_{_{ref}}}\right)}\; f\left(\frac{r}{\delta_{_{ref}}}\right).$$

Let us consider the free volume energy $g_{\rho_{_{ref}}}(\rho)$, null in the mother bulk of density $\rho_{_{ref}}$ (where $\rho_{_{ref}} = \rho_{l_b}$ or $\rho_{_{ref}} = \rho_{v_b}$) chosen as the reference mother bulk; the free energy ϕ per unit of volume in a inhomogeneous fluid is

$$\phi = g_{\rho_{_{ref}}}(\rho) + \frac{\lambda}{2}\,\left(\frac{d\rho}{dr}\right)^2$$

and consequently, if ϕ is expressed as a function of r,

$$\begin{aligned} \phi(r) &= g_{\rho_{ref}}\left(\rho_{_{ref}} + \frac{\delta_{_{ref}}\,\left(\gamma_1 - \gamma_2\,\rho_{_{ref}}\right) f\left(\frac{r}{\delta_{_{ref}}}\right)}{\lambda\, h\left(\frac{R}{\delta_{_{ref}}}\right) + \gamma_2\,\delta_{_{ref}} f\left(\frac{R}{\delta_{_{ref}}}\right)}\right) + \\ &\quad \frac{\lambda}{2}\left(\frac{\left(\gamma_1 - \gamma_2\,\rho_{_{ref}}\right)\, h\left(\frac{r}{\delta_{_{ref}}}\right)}{\lambda\, h\left(\frac{R}{\delta_{_{ref}}}\right) + \gamma_2\,\delta_{_{ref}}\, f\left(\frac{R}{\delta_{_{ref}}}\right)}\right)^2 . \end{aligned} \tag{12}$$

4.1 Impossibility of a two-phase fluid in a nanotube

Let us consider a nanotube simultaneously filled with liquid and vapour of the same fluid; an interface appears between the liquid and vapour phases. By reason of symmetry the liquid-vapour interface is a material surface represented by a cylindrical surface with the same axis as the nanotube. The interface has a positive surface energy γ_{lv} increasing the free energy of the fluid inside the

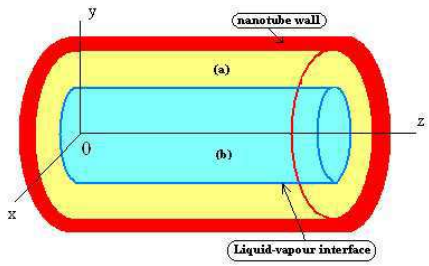

Figure 1: **Two-phase fluid in a nanotube**: The nanotube is simultaneously filled with two phases liquid and vapour of the same fluid. The two phases (a) and (b) are separated by a cylindric *material* interface.

nanotube.

First case: domain (a) *is liquid and domain* (b) *is vapour.* An approximation allows us to compare the energy of the only liquid phase and the energy of the two-phase fluid when the liquid is in contact with the nanotube wall. The free energies associated with the wall are approximatively equal. We have the relation $g_{l_b}(\rho) \equiv g_{v_b}(\rho) + g_{l_b}(\rho_{v_b})$ with $-g_{l_b}(\rho_{v_b}) = P(\rho_{v_b}) - P(\rho_{l_b}) = \Pi(\rho_{l_b})$; the term $\Pi(\rho_{l_b})$ is called *the disjoining pressure* relatively to the mother bulk ρ_{l_b} [11, 18].

The difference between the free energy per unit length E_1 of the liquid phase and the free energy per unit length E_2 of the two-phase fluid is approximatively

$$E_2 - E_1 = \pi \left(-e_1^2\, \Pi(\rho_{l_b}) + 2e_1\gamma_{lv}\right),$$

where e_1 denotes the radius of the domain (b) of vapour delimited by the interface. Consequently, the free energy for the two-phase fluid in the nanotube is smaller than for only the liquid phase if $e_1 \geq 2\gamma_{lv}/\Pi(\rho_{l_b})$.

Second case: domain (a) *is vapour and domain* (b) *is liquid.* We can also compare the energy of the only vapour phase and the energy of the two-phase fluid when the vapour is in contact with the nanotube wall. The free energies associated with the wall are approximatively equal.

The difference between the free energy per unit length E_3 of the vapour phase and the free energy per unit length E_4 of the two-phase fluid is approximatively

$$E_4 - E_3 = \pi \left(e_2^2\, \Pi(\rho_{l_b}) + 2e_2\gamma_{lv}\right),$$

where e_2 denotes the radius of the domain (b) of liquid delimited by the interface. Consequently, the free energy in the nanotube is smaller for the two-phase fluid than for the vapour phase if $e_2 \geq 2\gamma_{lv}/(-\Pi(\rho_{l_b}))$.

As an example, we consider the case of water at 20° Celsius, in **c.g.s.** units, the interfacial free energy $\gamma_{lv} = 72$. If $|\Pi(\rho_{l_b})| = 10^7$ (or 10 atmospheres),

corresponding to an important absolute value of the disjoining pressure, we obtain $e_1 = e_2 \geq R_0 = 14.4 \times 10^{-6} = 144$ nm$= 0.144\,\mu$m. Consequently, the nanotube is filled with only one phase if its radius verifies the inequality $R < R_0$. The limit radius R_0 corresponds to the radius of a microscopic tube. Consequently, we have just to compare the free energies of the liquid and the vapour phases filling up the nanotube.

4.2 Liquid phase in the nanotube

We consider the case when the fluid phase in the nanotube is liquid; the liquid density is close to ρ_{l_b} (and $\rho_{l_b} \simeq \rho_l$). We choose g_{l_b} as *reference level of volume free energy*. By taking account of Eq. (12) and $\delta_l = \sqrt{\lambda\rho_l/c_l^2}$, we get

$$\phi(r) = \frac{c_l^2}{2\rho_l}\left(\frac{\delta_l\,\left(\gamma_1 - \gamma_2\,\rho_{l_b}\right) f\left(\frac{r}{\delta_l}\right)}{\lambda\, h\left(\frac{R}{\delta_l}\right) + \gamma_2\,\delta_l f\left(\frac{R}{\delta_l}\right)}\right)^2 + \frac{\lambda}{2}\left(\frac{\left(\gamma_1 - \gamma_2\,\rho_{l_b}\right) h\left(\frac{r}{\delta_l}\right)}{\lambda\, h\left(\frac{R}{\delta_l}\right) + \gamma_2\,\delta_l\, f\left(\frac{R}{\delta_l}\right)}\right)^2 . \quad (13)$$

Due to the fact that $c_l^2\delta_l^2/2\rho_l = \lambda/2$, Eq. (13) reads

$$\phi(r) = \frac{\lambda}{2}\,\left(\gamma_1 - \gamma_2\,\rho_{l_b}\right)^2 \frac{f\left(\frac{r}{\delta_l}\right)^2 + h\left(\frac{r}{\delta_l}\right)^2}{\left(\lambda\, h\left(\frac{R}{\delta_l}\right) + \gamma_2\,\delta_l\, f\left(\frac{R}{\delta_l}\right)\right)^2} .$$

The total free energy per unit of length in the nanotube is:

$$E_{l_b}(\rho_{l_b}) = 2\pi\left(\int_0^R \phi(r)\, r\, dr + R\left(-\gamma_1 + \frac{\gamma_2}{2}\,\rho_{_R}\right)\rho_{_R}\right),$$

where

$$\rho_{_R} = \rho_{l_b} + \frac{\delta_l\,\left(\gamma_1 - \gamma_2\,\rho_{l_b}\right)}{\gamma_2\,\delta_l\, f\left(\frac{R}{\delta_l}\right) + \lambda\, h\left(\frac{R}{\delta_l}\right)} f\left(\frac{R}{\delta_l}\right).$$

Consequently, if we denote $r = \delta_l\, x$ and $n = R/\,\delta_l$, we obtain the total free energy per unit of surface in the nanotube $F_{l_b}(\rho_{l_b}) \equiv E_{l_b}(l)/2\pi R$ in the form

$$F_{l_b}(\rho_{l_b}) = \frac{\delta_l c_l^2}{2\rho_l}\frac{\left(\gamma_1 - \gamma_2\,\rho_{l_b}\right)^2}{n}\int_0^n \frac{f\,(x)^2 + h\,(x)^2}{\left(\gamma_2\, f\,(n) + \frac{\lambda}{\delta_l}\, h\,(n)\right)^2}\, x\, dx + \left(-\gamma_1 + \frac{\gamma_2}{2}\,\rho_{_R}\right)\rho_{_R}. \quad (14)$$

4.3 Vapour in the nanotube

We consider the case when the fluid phase in the nanotube is vapour; the vapour density is close to ρ_{v_b} (and $\rho_{v_b} \simeq \rho_v$). For the reference level of volume free energy we obtain for a density close to ρ_v

$$g_{l_b}(\rho) = \frac{c_v^2}{2\rho_v}\,(\rho - \rho_v)^2 - \Pi(\rho_{l_b}).$$

The density in the nanotube is close to the vapour density ρ_{v_b} and consequently we neglect the surface free energy of the wall. With $\gamma_1 - \gamma_2\,\rho_{v_b} \approx \gamma_1$ we get

$$\phi(r) \approx \psi(r) - \Pi(\rho_{l_b}) \quad \text{with} \quad \psi(r) = \frac{\lambda}{2}\,\gamma_1^2\,\frac{f\left(\frac{r}{\delta_v}\right)^2 + h\left(\frac{r}{\delta_v}\right)^2}{\left(\lambda\,h\left(\frac{R}{\delta_v}\right) + \gamma_2\,\delta_v\,f\left(\frac{R}{\delta_v}\right)\right)^2}\,,$$

where $\delta_v = \sqrt{\lambda\rho_v/c_v^2}$. The total free energy per unit of length in the nanotube is:

$$E_{l_b}(\rho_{v_b}) = 2\pi\left(\int_0^R \psi(r)\,r\,dr - \Pi(\rho_{l_b})\frac{R^2}{2}\right).$$

If we denote $r = \delta_v\,x$ and $N = R/\delta_v$, we obtain the total free energy per unit of surface in the nanotube $F_{l_b}(\rho_{v_b}) \equiv E_{l_b}(v)/2\,\pi\,R$ in the form

$$F_{l_b}(\rho_{v_b}) = \frac{\delta_v\,c_v^2}{2\rho_v}\frac{\gamma_1^2}{N}\int_0^N \frac{f\,(x)^2 + g\,(x)^2}{\left(\gamma_2\,f\,(N) + \frac{\lambda}{\delta_v}\,g\,(N)\right)^2}\,x\,dx \;-\; \frac{N\,\delta_v}{2}\,\Pi(\rho_{l_b})\,. \qquad (15)$$

4.4 Numerical application in the case of water

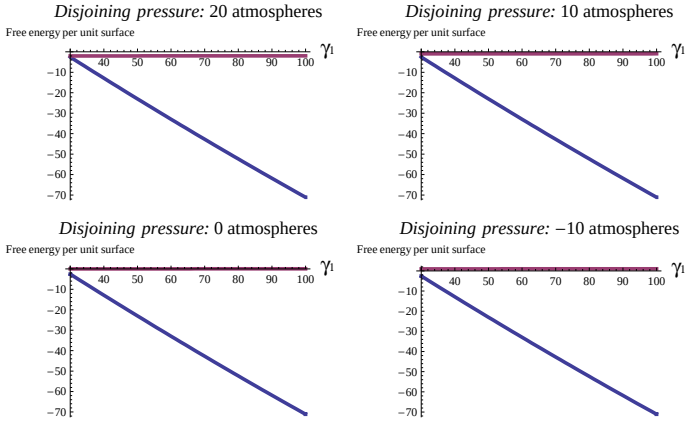

Figure 2: **Nanotube of diameter 4 nm**: When we change the value of the disjoining pressure $\Pi(\rho_{l_b})$, the total free energy in a nanotube filled up with liquid water phase is smaller than the total free energy of a nanotube filled up with vapour water phase. Consequently, the nanotube is always filled up with a liquid water phase.

In **c.g.s.** units the physical constants of water are $c_v = 3.7\ \times 10^4$; $c_l = 1.478\ \times 10^5$; $\rho_v = 1.7\ \times 10^{-6}$; $\rho_l = 0.998$; $\lambda = 1.17\ \times 10^{-5}$; $\gamma_2 = 54$.
We have obtained the free energy values for liquid and vapour phases. Relations

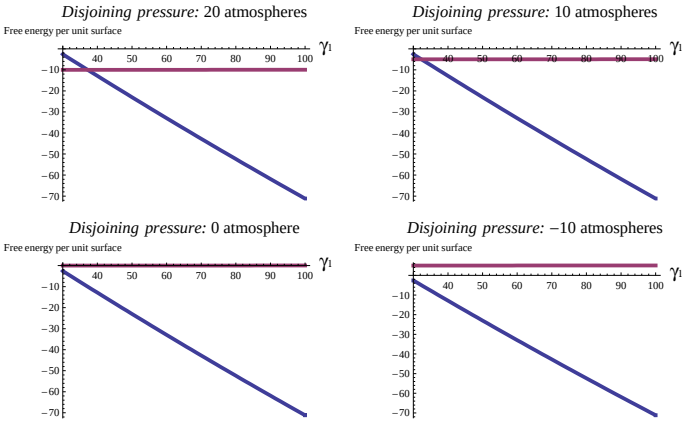

Figure 3: **Nanotube of diameter 20 nm**: When the disjoining pressure is positive and strong enough and if the wall is strongly hydrophobic, the nanotube can be filled up with a water vapour phase. For an hydrophillic wall the nanotube is always filled up with a liquid water phase.

(14-15) depend on both the wetting quality of the wall and on the value of the disjoining pressure. For convenient materials, we can numerically compare the free energy of the liquid with the free energy of the vapour. We consider the case when the water fluid is in contact with different nanotube walls. The x-axis corresponds to the value of γ_1 associated with the hydrophobicity or hydrophillicity of the wall. The value of γ_2 depends only on the fluid. When γ_1 is small enough, the wall of the nanotube is hydrophobic and when γ_1 is large enough, the wall of the nanotube is hydrophillic. The y-axis corresponds to the value of the total free energy in the nanotube per unit surface of the wall. The case when the nanotube wall is strongly hydrophobic corresponds to $\gamma_1 < 30$. In all the graphs the straight line parallel to the x-axis corresponds to the free energy per unit surface of the nanotube filled up with a vapour phase; the oblique curve corresponds to the free energy per unit surface of the nanotube filled up with a liquid phase. The graphs corresponding to the values of the two free energies (14-15) allow to foresee if the nanotube is filled up with liquid or with vapour. They are presented in Figures 2 to 4.
When the disjoining pressure is negative, the nanotube is filled up with a liquid water phase for all diameters of the nanotube. When the nanotube wall is hydrophobic, for a large radius and a strong positive disjoining pressure, the nanotube can be filled up with a vapour phase. As a result, the case of vapour phase filling up the nanotube is less usual than the case of liquid water phase.
In all the cases, we note that the volume free energy of the phase in the nanotube is negligible with respect to the surface free energy of the wall.

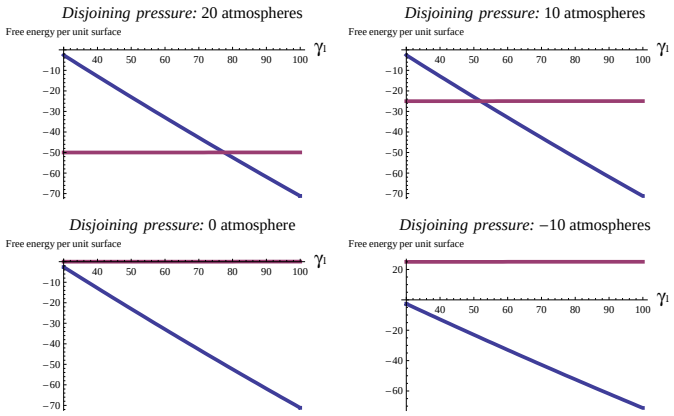

Figure 4: **Nanotube of diameter 100 nm**: The tube corresponding to a diameter of about $0.1\,\mu$m is a microtube. The quality of the wall and the effect of the disjoining pressure are in competition. If the disjoining pressure is strong enough and if the wall is moderately hydrophobic, the tube is filled up with vapour water phase. When the disjoining pressure is negative, the tube is always filled up with liquid water phase.

5 Permanent viscous motions in a nanotube

"Fluid flow through nanoscopic structures, such as carbon nanotubes, is very different from the corresponding flow through microscopic and macroscopic structures. For example, the flow of fluids through nanomachines is expected to be fundamentally different from the flow through large-scale machines since, for the latter flow, the atomistic degrees of freedom of the fluids can be safely ignored, and the flow in such structures can be characterized by viscosity, density and other bulk properties. Furthermore, for flows through large-scale systems, the no-slip boundary condition is often implemented, according to which the fluid velocity is negligibly small at the fluid/wall boundary. Reducing the length scales immediately introduces new phenomena into the physics of the problem, in addition to the fact that at nanoscopic scales the motion of both the walls and the fluid, and their mutual interaction, must be taken into account" [30].

In this section, we consider the permanent and laminar motions of viscous capillary liquid in a nanotube. Because the liquid is heterogeneous, for capillary fluids, the liquid stress tensor is not anymore scalar and the equations of hydrodynamics are not valid. However, the results obtained for viscous flows [24] can be adapted at nanoscale.
As in [31], we assume that the kinematic viscosity coefficient $\nu = \kappa/\rho$ only depends on the temperature. In the equation of motions, the viscosity term is

$$(1/\rho)\,\mathrm{div}\,\boldsymbol{\sigma}_v = 2\nu\,[\,\mathrm{div}\,\boldsymbol{D} + \boldsymbol{D}\,\mathrm{grad}\,\{\,\mathrm{Ln}\,(2\,\kappa)\}\,]\,,$$

where $\boldsymbol{D}$ is the velocity deformation tensor and $\boldsymbol{D}$ grad$\{\text{Ln}\,(2\,\kappa)\}$ is negligible with respect to div $\boldsymbol{D}$.
We denote the velocity by $\mathbf{V} = (0, 0, w)^T$ where w is the velocity component in direction of the nanotube axis. When we neglect the external forces (as gravity), the liquid nano-motion verifies Eq. (6) written in the form

$$\mathbf{a} + \text{grad}[\,\mu_o(\rho) - \lambda\,\Delta\rho\,] = \nu\,\Delta\mathbf{V} \quad \text{with} \quad \Delta\mathbf{V} \simeq \left[0, 0, \Delta w\right]^T . \tag{16}$$

Simple fluids slip on a solid wall only at a molecular level [7] and consequently, in classical conditions, the kinematic condition at solid wall is the adherence condition ($z = 0 \;\Rightarrow\; w = 0$). Recent papers in nonequilibrium molecular dynamic simulations of three dimensional micro-Poiseuille flows in Knudsen regime reconsider micro-channels: the influence of gravity force, surface roughness, surface wetting condition and wall density are investigated. The results point out that the no-slip condition can be observed for Knudsen flow when the surface is rough. The roughness is a dominant parameter when the slip of fluid is concerned. The surface wetting condition substantially influences the velocity profiles [33]. But it is not the case for smooth surfaces. The relation between wall shear stress and slip velocity is the key for characterizing the slip flow. With water flowing through hydrophobic thin capillaries, there are some qualitative evidences for slippage [4]. De Gennes said: "the results are unexpected and stimulating and led us to think about unusual processes which could take place near a wall. They are connected with the thickness of the film when the thickness is of an order of the mean free path" [10].
When the free mean path L is smaller than d, the Knudsen number Kn is smaller than 1. That is the case for liquid where the mean free path L is of the same order than the molecular diameter. For example in the case of liquid water, Kn ranges between 0.5 and 10^{-2} while the nanotube radius ranges between 1 nm and 50 nm. The adherence boundary condition at a surface, commonly employed with the Navier-Stokes equation assuming a zero flow, is physically invalid and a slip regime occurs; the boundary condition must be changed to take account of the slippage at the solid surfaces.
For gases, the mean free path is of order of one hundred molecular diameters and consequently the flow regime is only valid for large nanotubes. For thin nanotubes the rarefied gas regime must be considered; but the calculation in slip regime may give an idea of the change of flow with respect to the Navier-Stokes regime also for gases. Nonetheless, we note that the vapour phase in the tube occurs for large nanotube relevant from the microfluidic case and the slip condition using continuum mechanics is realistic. In fluid/wall slippage, the condition at solid wall writes

$$w = L_s \frac{\partial w}{\partial r} \qquad \text{at} \quad r = R, \tag{17}$$

where L_s is the so-called Navier length [24]. The Navier length is expected to be independent of the thickness of the nanoflow and may be as large as a few microns [33].

In the following, the dynamics of liquid nanoflows is studied in the case of nonrough nanotubes. Consequently,
i) The equation of motion writes in the form (16),
ii) The boundary conditions take account of the slip condition (17).
When the liquid nanoflow thickness is small with respect to transverse dimensions of the wall, it is possible to simplify Eq. (16) which governs the viscous flow; so, when $d \ll \ell$,
iii) We consider a laminar flow: the velocity component along the wall is large with respect to the normal velocity component to the wall which is negligible.
iv) For permanent motion, the equation of continuity reads:

$$(\mathtt{grad}\,\rho)^T\,\mathbf{V} + \rho\ \mathtt{div}\,\mathbf{V} = 0.$$

The velocity vector $\mathbf{V}$ mainly varies along the direction orthogonal to the wall and $\mathrm{grad}\,\rho$ is normal to $\mathbf{V}$. The density is constant along each stream line ($\dot{\rho} = 0 \Longleftrightarrow \mathtt{div}\,\mathbf{V} = 0$); the trajectories are drawn on isodensity surfaces and $w = w(r)$. Due to the solid wall effect, the density in the tube is closely constant out from a boundary layer of approximatively one nanometer [18]; consequently, we consider the approximation of an incompressible liquid in the tube.
v) Due to the geometry of the tube, for permanent motion, the acceleration is null. Equations (6) or (16) separate as:

- The first part along the z-coordinate,

$$\frac{\partial P}{\partial z} = \kappa\,\Delta\, w \qquad \text{with} \qquad \Delta\, w = \frac{1}{r}\frac{d}{dr}\left(r\ \frac{dw}{dr}\right), \tag{18}$$

- The second part in the plane orthogonal to the tube axis,

$$\frac{\partial}{\partial r}\left(\lambda\,\Delta\rho - \mu_{_0}\right) = 0. \tag{19}$$

Equation (19) yields the same equation (10) as at equilibrium. Equation (18) yields

$$\frac{1}{r}\frac{d}{dr}\left(r\ \frac{dw}{dr}\right) = -\frac{\wp}{\kappa}\,, \tag{20}$$

where $\wp$ denotes the pressure gradient along the nanotube. The cylindrical symmetry of the nanotube yields the solution of Eq. (20) in the form

$$w = -\frac{\wp}{\kappa}\,\frac{r^2}{4} + b,$$

where b is constant. Condition (17) implies

$$-\frac{\wp}{4\kappa}R^2 + b = L_s\frac{\wp}{2\kappa}R$$

and consequently,

$$w = \frac{\wp}{4\kappa}\left(-r^2 + R(R + L_s)\right).$$

The density in the nanotube is closely equal to ρ_l and the volume flow through the nanotube is $Q = 2\pi \int_0^R w\, r\, dr = \frac{\pi\, \wp}{8\, \kappa} R^3(R + 4L_s)$. With Q_o denoting the Poiseuille flow corresponding to a tube of the same radius R, we obtain:

$$Q = Q_o \left(1 + \frac{4L_s}{R}\right). \tag{21}$$

In most cases, the Navier length is of the micron order ($L_s = 1\,\mu m = 10^3\,\text{nm}$) [25]. If we consider a nanotube with $R = 2\,\text{nm}$, we obtain $Q = 2 \times 10^3\, Q_o$. For $R = 50\,\text{nm}$, that we consider as the maximum radius of nanotube with respect to microfluidics, we obtain $Q = 40\, Q_o$. Consequently, the flow of liquid in nanofluidics is dramatically more important than the Poiseuille flow in cylindrical tubes. In the case of gases, we obtain the same results for nanotube of radius $R = 50\,\text{nm}$ corresponding to a Knudsen number smaller than 0.5. For nanotubes of radius smaller than 30 nm, when the nanotube is unusually filled up with a vapour phase, the flow is not anymore a continuous flow but is relevant to kinetic of rarified gases. Nevertheless, the magnitude of this flow is of several order more important than Poiseuille flow.
We have to emphasis that, when the mother bulk is vapour, in classical Poiseuille flow, the phase is vapour in the tube but, for a nanotube the phase is generally liquid (as in conditions presented in Fig. 2 and Fig. 3) and the volume flow through the nanotube is approximatively:

$$Q = Q_o \frac{\rho_l}{\rho_v} \left(1 + \frac{4L_s}{R}\right).$$

In the case of water $\rho_l/\rho_v \sim 10^3$, we get a volume flow 10^3 time more important than the volume flow obtained in Eq. (21):

$$Q \sim 10^6\, Q_o\,.$$

6 Conclusion

A nanotube with a diameter ranging between 4 and 100 nanometres is filled up only with one liquid phase or one vapour phase independently of the external mother bulk. For nanotubes with diameters smaller than 20 nm, the fluid phase inside the nanotube is generally liquid. For nanotubes of large diameters with respect to the molecular scale, the fluid phase can be liquid or vapour according to the values of the disjoining pressure and of the physicochemical properties of the tube walls.
For nanotubes with small diameters, the flows can be significantly greater than usual Poiseuille flows, especially if the mother bulk consists of vapour.
These results, obtained by using a nonlinear model of continuum mechanics and its associated differential equations, are in good agreement with experiments and molecular dynamics calculations.

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